

Reduction of CO₂ by Hydrosilanes in the Presence of Formamidinates of Group 13 and 12 Elements

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Cite This: <https://dx.doi.org/10.1021/acs.organomet.9b00853>

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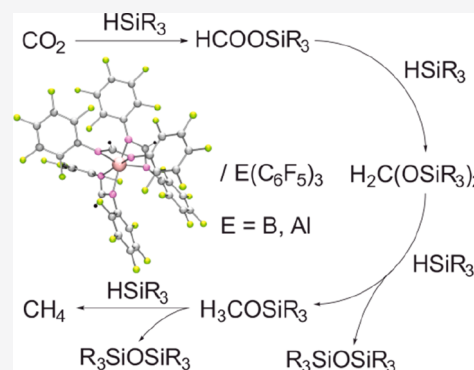
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ABSTRACT: Homoleptic complexes **1-M** of group 13 and 12 elements (M = B–In and M = Zn, respectively) incorporating electron-withdrawing formamidinate ligands $\{(C_6F_5)_3N=CHN(C_6F_5)\}^-$ ($\{NCN\}^-$) were synthesized and isolated in high yields. The compounds were characterized by X-ray crystallography, NMR spectroscopy, and elemental analysis. While the single-component **1-M** appeared to be sluggishly active or inactive in the reduction of CO₂ with hydrosilanes, a good catalytic performance was achieved with the two-component systems derived from combinations of **1-M** and E(C₆F₅)₃ (E = B, Al). In particular, the binary combination **1-Al**/B(C₆F₅)₃ showed the best performance within the whole series, thus providing quantitative hydrosilane (Et₃SiH) conversions under a range of conditions (*P*_{CO₂}, temperature, benzene or bromobenzene solvent) and affording mainly CH₂(OSiEt₃)₂ and CH₄ as products. Kinetic and mechanistic studies revealed that at the initiation step the binary catalytic systems undergo a complex transformation in the presence of CO₂/Et₃SiH, affording the products of **1-Al** decomposition: namely, (C₆F₅)N(H)SiEt₃, (C₆F₅)N(Me)SiEt₃, {NCN}SiEt₃, and also some unidentified aluminum species. Thus, the overall process of the reduction of CO₂ with hydrosilanes is presumed to be catalyzed by complex multisite systems, evolved from the formamidinate precursor **1-Al**, implicating different tandem combinations of N-base/B(C₆F₅)₃ with putative Al-containing species.



INTRODUCTION

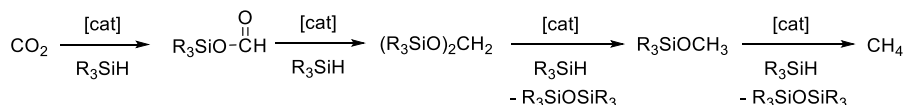
Catalytic reduction of CO₂ with hydrosilanes as a source of hydrogen has regained attention in recent years.¹ In contrast to the industry-relevant processes involving utilization of hydrogen as a reducing agent,² the application of highly energetic hydrosilanes enables reduction of CO₂ under significantly milder conditions due to the thermodynamic stability of the corresponding products incorporating Si–O bonds. While late-transition-metal-based catalysts from various groups (7–11)^{1,3} traditionally play a dominant role in CO₂ hydrosilylation, some other examples have emerged very recently involving main-group-metal organometallics (Zn,⁴ group 13 (Al and Ga)⁵) or metal-free systems such as Lewis acids (e.g., BPh₃),⁶ frustrated Lewis pairs (FLP),^{7,8} phosphazenes,⁹ formate organocatalysts,¹⁰ and abnormal N-heterocyclic carbene.¹¹ In addition, both tandem and FLP-like catalytic systems were developed, which are based on binary combinations of a main-group-metal or transition-metal precursor and a strong Lewis acid (typically B(C₆F₅)₃): Mg/B(C₆F₅)₃,¹² Zn/B(C₆F₅)₃,¹³ Al/B(C₆F₅)₃,¹⁴ Sc/B(C₆F₅)₃,¹⁵ Zr/B(C₆F₅)₃,¹⁶ Re/B(C₆F₅)₃,¹⁷ and Ni/Et₃B and Pd,Pt/R₃B (R = Ph, C₆F₅).¹⁸ Depending on the nature of the silane, the type of catalytic system involved, and conditions, the reduction process can be halted at a desired step, thus allowing preparation with high selectivity of one of the targeted products (Scheme 1) exhibiting a different degree of reduction of the carbon atom: silyl formate,^{3a,b,d,e,g–k,m,4c,9b,10,11,18b}

bis(silyl)acetal,^{3b,6,12,13b,17,15a} methoxysilane^{3m,4d,5b,9a,13a,15a} and finally methane.^{3g,5a,7,13–16,18a}

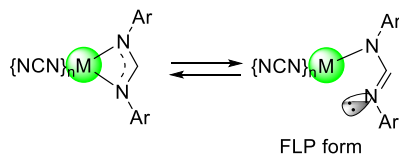
In this work, a new series of homoleptic complexes of group 13 (B, Al, Ga, In) and group 12 elements (Zn) incorporating *N,N'*-bis(perfluorophenyl)formamidinate ligands have been prepared and their behavior as catalysts in hydrosilylation of CO₂ was studied. We initially hypothesized that during the catalytic process the bidentate LX-type formamidinate ligands¹⁹ {NCN}[−] in the complexes undergo a partial decoordination/rearrangement into an imino-amido form, providing a N-centered Lewis base function in the close proximity to the vacant Lewis acidic group 13/12 element center and thus giving rise to a FLP form (Scheme 2).²⁰ Then, the latter species could presumably trigger the CO₂ hydrosilylation mechanism, enabling both fixation of CO₂²¹ and activation of hydrosilane²² on the two cooperating centers and thus promoting the formation of silyl formate. While discouraging catalytic performance in hydrosilylation of CO₂ was initially observed upon utilization of the formamidinate complexes, their binary combinations with E(C₆F₅)₃ (E = B,

Received: December 18, 2019

Scheme 1. Fundamental Steps and Products of Catalytic Reduction of CO₂ with Hydrosilane R₃SiH



Scheme 2. Formation of a FLP Form

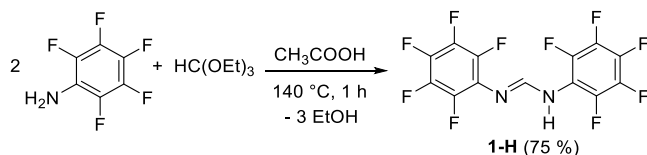


Al) appeared to be more efficient catalytic systems. Unexpectedly, very different reactivity patterns were identified for these two-component systems, which are related to the catalyst transformation processes operating under the catalytic conditions.

RESULTS AND DISCUSSION

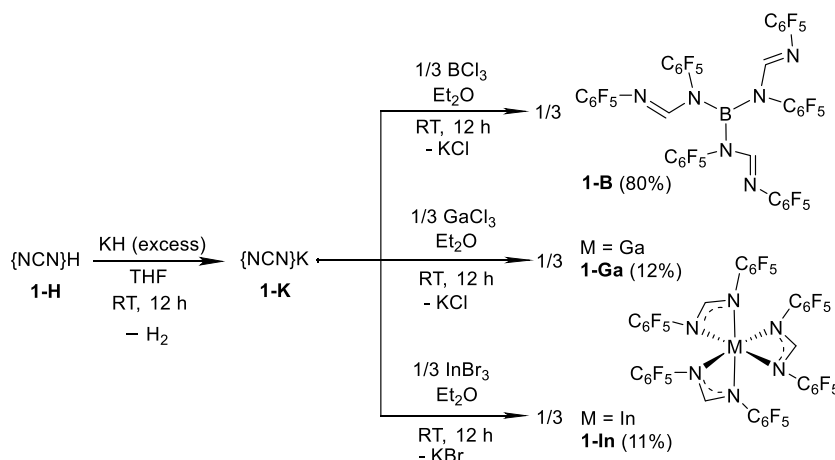
Synthesis of Proligand *N,N'*-Bis(pentafluorophenyl)methanimidamine (1-H**).** The introduction of electron-withdrawing groups in a ligand platform constitutes a general way to increase the electropositivity and, thus, the reactivity of the active center of a Lewis acid catalyst. Therefore, the use of a poorly donating amidinate-type ligand incorporating C₆F₅ substituents on the electronegative nitrogen atoms was sought in this study. The corresponding proligand **1-H** was prepared and isolated in 75% yield using the reported synthetic procedure (Scheme 3).²³ The molecular structure of **1-H** (benzene) is shown in Figure S1.²⁴

Scheme 3. Synthesis of Proligand **1-H**



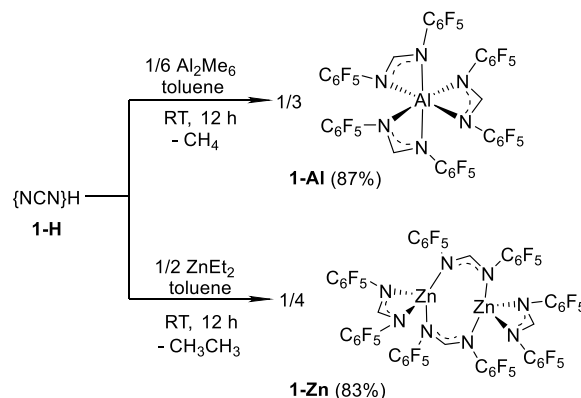
Synthesis of Complexes of B, Al, Ga, In, and Zn. Deprotonation of **1-H** with KH in THF resulted in the formation of the corresponding monoanionic potassium salt **1-K**

Scheme 4. Synthesis of Complexes **1-B,Ga,In** by Salt Metathesis



K (Scheme 4), which was used without isolation in a regular salt-metathesis reaction to prepare the complexes of general formula M{NCN}₃ (M = B (**1-B**), Ga (**1-Ga**), In (**1-In**)). On the other hand, complexes **1-Al,Zn** were conveniently prepared by one-step alkane elimination reactions between the corresponding metal–alkyl reagent and **1-H** proligand (Scheme 5). Compounds **1-B,Zn** are soluble in diethyl ether,

Scheme 5. Synthesis of Complexes **1-Al,Zn** by σ -Bond Metathesis



toluene, benzene, bromobenzene, and dichloromethane, while **1-Al,Ga,In** exhibit a relatively low solubility in the solvents mentioned above. All complexes are insoluble in aliphatic solvents (heptane and hexane). **1-B** appeared to be unstable in THF, rapidly polymerizing this solvent, presumably by a cationic mechanism.²⁵ All of the compounds were characterized by NMR spectroscopy, X-ray crystallography, and elemental analysis.

Solid-State and Solution Structures of Complexes **1-B,Al,Ga,In,Zn.** The solid-state structures of complexes **1-B,Al,Ga,In,Zn** were established by X-ray diffraction studies (Figures 1–3, Table 1, and Table S1).

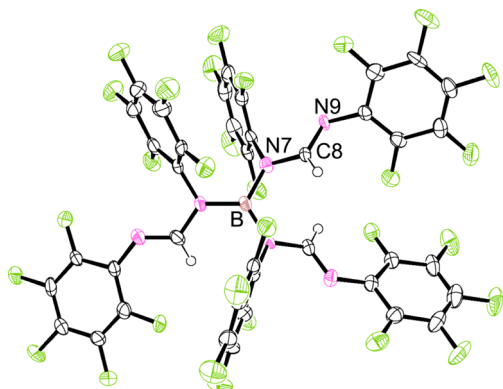


Figure 1. Molecular structure of **1-B** (thermal ellipsoids drawn at 50% probability).

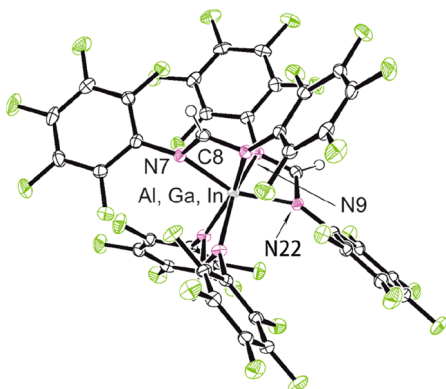


Figure 2. Molecular structures of **1-Al**, **1-Ga**, and **1-In** (benzene) (all solvent molecules omitted for clarity; thermal ellipsoids drawn at 50% probability).

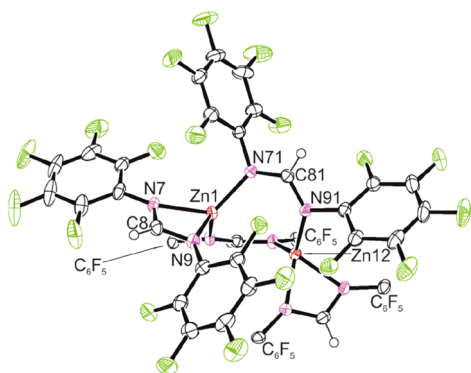


Figure 3. Molecular structure of **1-Zn·2(toluene)** (all solvent molecules and four C_6F_5 groups omitted for clarity; thermal ellipsoids drawn at 50% probability).

The crystal cell of **1-B** contains two crystallographically independent molecules differing in the reciprocal orientation of the three ligands; thus, only one was selected for analysis and discussion. The boron atom in **1-B** (Figure 1) features a planar-trigonal coordination environment, provided by the equivalent monoanionic imine-formamido ligands each bound with only one nitrogen atom.²⁶ Therefore, the coordination of the ligands is different from the regular η^2 mode previously observed in amidinate compounds of the type $\{\eta^2\text{NCN}\}BX_2$ ($X = C_6F_5$,^{20a,b} Cl²⁷). Also, the C8–N9 bonds (1.265(7)–1.273(7) Å) in the ligand fragments are shortened and the

C8–N7 bonds (1.390(8)–1.399(8) Å) are elongated in comparison to those in the neutral proligand (1.314(2) and 1.315(2) Å, respectively), which is the result of a preferential negative charge localization on the N7 atom in this formal imine-formamido ligand. The B–N distances in **1-B** (1.449(8)–1.462(8) Å) are on the longer side of the range observed for those in typical boron-anilido complexes $B(NMePh)_3$ and $B(NHPh)_3$ (1.428–1.442 Å).²⁸ Also, the molecule exhibits a short F...B contact (2.915(7) Å) with one *o*-F atom of the closest C_6F_5 aryl ring.

The X-ray crystallographic study for **1-Al,Ga,In** (Figure 2) revealed them to be isostructural species, each featuring the corresponding metal center, chelated by three slightly asymmetrically bound amidinate ligands, in a six-coordinate distorted-octahedral environment. Thus, the difference between the corresponding M–N bond lengths within the same amidinate ligand does not exceed 0.05 Å. Within the series **1-Al,Ga,In**, the M–N bond distances are elongated, which is in line with the increase of the effective ionic radii of the M^{3+} metal ions.²⁹ In **1-Al**, the M–N bond lengths (1.986(1)–2.021(1) Å) are in the normal range of those observed in various amidinate complexes of aluminum (1.884–2.066 Å).^{30,31} At the same time, in the congeners **1-Ga** and **1-In**, the corresponding M–N distances (2.022(3)–2.111(3) and 2.214(1)–2.264(1) Å, respectively) are on the longer side of those reported for their respective analogues (1.996–2.019 and 2.181–2.244 Å, respectively).³⁰

The molecular structure of **1-Zn** (Figure 3) consists of a centrosymmetric dimer, in which the two $\{\eta^2\text{-NCN}\}Zn$ moieties are bound by the two μ_2 -bridging monoanionic NCN fragments in a “spanned” manner. Thus, each zinc atom has a formal coordination number of 4 and features a distorted-tetrahedral environment. The Zn–N distances in **1-Zn** are very close to those observed in the relevant complexes incorporating both terminal and bridging $\{\text{NCN}\}^-$ ligands (2.002–2.092 and 2.000–2.070 Å, respectively).³²

The solution structures of the compounds were also established by NMR spectroscopy. The room-temperature ^1H NMR spectra of compounds **1-B,Al,Ga,In,Zn** (Figures S2, S7, S10, S12, and S15, respectively), recorded in C_6D_6 or in C_7D_8 , exhibited in each case a single resonance from the methine $=\text{CH}-$ protons of the formamidinate ligands. Similarly, the corresponding single resonances of the methine carbons were observed in the room-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the compounds **1-B,Al,In** in CD_2Cl_2 and that of **1-Zn** in C_6D_6 (Figures S6, S9, S14, and S17, respectively). For an unclear reason, no signals from the complex were observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at different temperatures of several independently prepared samples of **1-Ga**. In the $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **1-Al,Ga,In** (Figures S8, S11, and S13, respectively), a regular set of narrow signals including one doublet and two triplets from the corresponding *o*-F, *p*-F, and *m*-F groups was observed. Therefore, the NMR data obtained for compounds **1-Al,Ga,In** are consistent with their solid-state structures in which the three equivalent formamidinate ligands bind the metal center in an average symmetrical fashion.

In striking contrast with **1-Al,Ga,In**, compounds **1-B,Zn**³³ featured a complex fluxional dynamic behavior in solution over a broad temperature range. For **1-B**, the broadened singlet from the methine protons in the ^1H NMR in toluene- d_8 sharpened upon heating to 80 °C (Figure 4), whereas when the temperature was decreased to –70 °C, the latter signal decoalesced into a series of very broad signals. Also, the three

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1-H,B,Al,Ga,In,Zn

	1-H	1-B	1-Al	1-Ga	1-In	1-Zn
M–N7 ^a		1.444(8)	2.015(1)	2.022(3)	2.214(1)	2.050(2)
		1.453(8)	2.017(1)	2.022(3)	2.214(1)	2.050(2)
		1.462(8)	2.021(1)	2.111(3)	2.264(1)	
M–N9			1.986(1)	2.083(3)	2.260(1)	2.069(2)
			1.996(1)	2.083(3)	2.260(1)	2.069(2)
			2.002(1)	2.111(3)	2.264(1)	
M–N71						1.977(2)
						1.977(2)
M–N91						1.985(2)
						1.985(2)
N71–C78						1.319(3)
						1.319(3)
N7–C8–N9	121.4(2)	120.3(5)	111.7(1)	111.7(3)	114.8(2)	113.00(2)
N71–C81–N91						124.10(2)
N7–M–N22			159.4(1)	166.8(3)	168.8(2)	
N7–M–N71						103.8(8)

^aM = metal/element center.

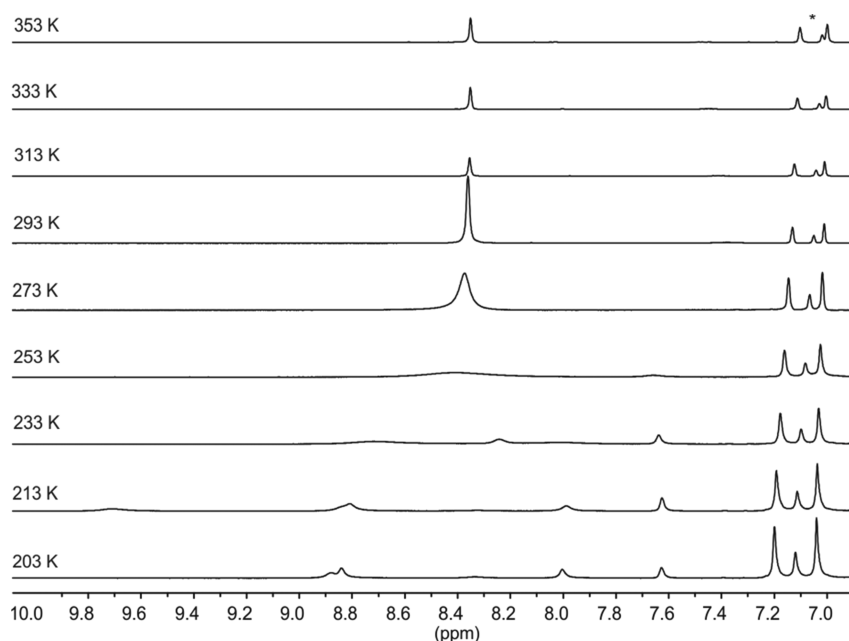


Figure 4. Stack plot of ¹H NMR spectra (400 MHz, toluene-*d*₈) of 1-B at different temperatures (the asterisk denotes a residual solvent signal).

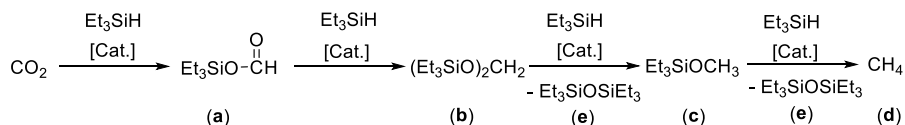
Table 2. DFT Calculated HOMO–LUMO Gaps, Dipole Moments, and NBO Charges and Experimentally Measured $\Delta\delta$ (³¹P) and AN Values for B(C₆F₅)₃ and 1-B,Al,Ga,In,Zn^a

	B(C ₆ F ₅) ₃	1-B	1-Al	1-Ga	1-In	1-Zn
<i>E</i> _{HOMO} (eV)	−7.08	−6.31	−7.26	−6.19		−5.99
<i>E</i> _{LUMO} (eV)	−2.97	−2.17	−3.92	−1.59		−1.51
HOMO–LUMO gap (eV)	4.11	4.14	3.34	4.60		4.48
dipole moment (D)	0.03	3.24	0.18	0.23		1.07
NBO charge on M (e)	0.834	1.199	1.897	1.694		1.303
$\Delta\delta$ (³¹ P) (ppm) ^b	30.0 ^c	33.0	4.7	33.4	23.6	17.7
AN ^d	76.0	82.9	20.4	83.7	62.0	48.9

^aB3PW91/6-31G(d,p), SMD (toluene). ^bThe difference between the ³¹P{¹H} NMR chemical shifts of the free Et₃P=O and that of its adduct with the substrate measured in benzene-*d*₆ at room temperature. ^cThe reported value in C₆D₆ at room temperature is 30.2 ppm.³⁷ ^dCalculated using the expression AN = 2.21(δ (³¹P)_{LA-Et₃PO} − 41).³⁸

broadened multiplets observed in the ¹⁹F{¹H} NMR spectrum taken at room temperature, upon cooling to −70 °C, split into a complicated series of overlapping multiplets (Figure S4).

These observations are indicative of a ligand rearrangement process in the coordination sphere of boron in 1-B and/or of atropoisomerism. Being very slow or frozen at low temper-

Scheme 6. Products of the Catalytic Reduction of CO₂ with Et₃SiHTable 3. Catalytic Reduction of CO₂ with Et₃SiH in the Presence of 1-B^a

entry	precat. (mol %)	silane/conversn (%) ^b	solvent	P _{CO₂} (bar)	T (°C)	t (h)	Si product conversn (%) ^c				
							a	b	c	d	f + g
1 ^d	1-B (0.5)	Et ₃ Si-H/0	C ₇ D ₈	1	25	48	0	0	0	0	0
2 ^d	1-B (0.5)	Et ₃ Si-H/0	C ₇ D ₈	1	80	16	0	0	0	0	0
3	1-B (10)	Et ₃ Si-H/6	C ₆ D ₃ Br	1	80	48	0	5.1	0	0	0
4	1-B (5.0), B(C ₆ F ₅) ₃ (5.0)	Et ₃ Si-H/18	C ₆ D ₃ Br	1	80	5	0	1.5	0.5	2.1	8.3
5	1-B (5.0), B(C ₆ F ₅) ₃ (5.0)	Et ₃ Si-H/36	C ₆ D ₃ Br	1	80	48	0	11.0	0.6	8.1	9.1
6 ^e	1-B (5.0), B(C ₆ F ₅) ₃ (5.0)	Et ₃ Si-H/46	C ₆ D ₃ Br	6	80	5	0	7.9	0.7	22.5	8.8
7 ^e	1-B (5.0), B(C ₆ F ₅) ₃ (5.0)	Et ₃ Si-H/>98	C ₆ D ₃ Br	6	80	25	0	12.1	1.1	69.1	10.7
8	1-B (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/18	C ₆ D ₃ Br	1	80	5	0	2.3	0	0.8	6.0
9	1-B (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/38	C ₆ D ₃ Br	1	80	48	0	5.9	0	11.4	8.5
10 ^e	1-B (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/38	C ₆ D ₃ Br	6	80	5	0	17.8	0	1.3	7.4
11 ^e	1-B (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/95	C ₆ D ₃ Br	6	80	48	0	17.7	0	54.2	9.3
12 ^e	1-B (10.0), tBu ₃ P (10.0)	Et ₃ Si-H/0	C ₆ D ₃ Br	6	80	48	0	0	0	0	0

^aReaction conditions, unless otherwise stated: solvent (0.5 mL), [Si-H]₀ = 0.26 mol L⁻¹, [cat.]₀ = 0.013 mol L⁻¹, n(CO₂) = 1.3 × 10⁻⁴ mol, internal standard (hexamethylbenzene) 0.0616 mol L⁻¹. ^bConversion of hydrosilane determined by the integration of the ¹H NMR resonances vs those of the standard, hexamethylbenzene. ^cYield of Si product determined by the integration of the corresponding ¹H NMR peak vs those of the standard, hexamethylbenzene. ^dSolvent (5.0 mL). ^eSolvent (0.1 mL), [Si-H]₀ = 0.54 mol L⁻¹, [cat.]₀ = 0.054 mol L⁻¹, n(CO₂)₀ = 3.2 × 10⁻⁴ mol, internal standard (hexamethylbenzene) 0.0615 mol L⁻¹.

ature, both ligand exchange phenomena can afford a mixture of isomers incorporating three- or four-coordinated boron centers and featuring different ligand binding motifs and symmetries.

A similar process of the ligand rearrangement is apparently operational for the dinuclear 1-Zn,³³ thus resulting in a rapid exchange at room temperature and the observation of an average symmetric species in the corresponding NMR spectra (Figures S15–S17).

Evaluation of Lewis Acidity and Acceptor Number (AN). A comparative analysis of the Lewis acidic character of the boron center in 1-B with respect to that of B(C₆F₅)₃ was performed by both theoretical (DFT) and experimental (NMR spectroscopy) techniques (Table 2). In fact, the somewhat higher Lewis acidic character of 1-B in comparison to that of B(C₆F₅)₃ is in line with the higher positive NBO charge on the boron atom (1.199 vs 0.834 e, respectively). At the same time, the observed higher Lewis acidity of 1-B cannot be explained by the calculated energy value of the π* orbital (E_{LUMO} - 2.17 eV), which should have been lower for a more Lewis acidic species.³⁴

The relative Lewis acidities of 1-B and B(C₆F₅)₃ were probed using an experimental Gutmann–Beckett³⁵ approach based on measuring the difference between the ³¹P{¹H} NMR chemical shift of the free Et₃P=O (δ 45.7) and that of the corresponding Lewis acid adduct. The 1-B/Et₃P=O system showed a greater Δδ(³¹P) difference (33.0 ppm) in comparison to the B(C₆F₅)₃/Et₃P=O reference (Δδ = 30.0 ppm), thus corroborating a higher Lewis acidity of the boron center in 1-B. In terms of AN, the Lewis acidity of 1-B is comparable with those of the catechol ester B(C₆F₅)(O₂C₆H₄) (AN = 81.5) and HB(2,4,6-(CF₃)₃C₆H₂) (AN = 83.3) and is lower than those of B(C₆F₅)₂(OC₆F₅) (AN = 86.2) and B(C₆F₅)(OC₆F₅)₂ (AN = 87.3).^{36–38}

Measurements of the differences in chemical shifts (Δδ(³¹P)) upon reaction between Et₃P=O and 1-M (M = Al, Ga, In, Zn), carried out under identical conditions, afforded the following relative order of Lewis acidities: 1-Al < 1-Zn < 1-In < B(C₆F₅)₃ < 1-B ≤ 1-Ga. Unexpectedly, the experimentally determined order of the Lewis acidities of 1-M (M = Al, Ga, In, Zn) stays in variance with the trend of computed NBO charges. For instance, the softest Lewis acid 1-Al within the whole series exhibited the greatest NBO charge on the aluminum center (1.897 e).

Catalytic CO₂ Hydrosilylation. Hydrosilylation of CO₂ with Et₃SiH in the presence of 1-B, Al, Ga, In, Zn was investigated. Strong Lewis acids, namely B(C₆F₅)₃ and Al(C₆F₅)₃(toluene)_{0.5}, were studied as catalysts for benchmarking purposes and then as cocatalysts¹⁴ in a tandem combination with 1-B, Al, Ga, In, Zn. For the best-performing catalytic systems, several parameters were examined such as the pressure of CO₂ (1 bar (n(CO₂)₀/n(Si-H)₀ = 1/1) and 6 bar (n(CO₂)₀/n(Si-H)₀ = 6/1)),³⁹ temperature, reaction time, the nature of the solvent (benzene vs bromobenzene), and the concentration of the precatalyst. In addition, hydrosilylation using different hydrosilanes (PhSiMe₂H, Ph₂SiH₂, PhSiH₃, Ph₃SiH, and (EtO)₃SiH) was also explored. The reactions were monitored by ¹H NMR spectroscopy, allowing detection of the formation of the four consecutive products (Scheme 6, a–d).⁴⁰ Formation of disiloxane Et₃SiOSiEt₃ (Scheme 6, e), the second product of the last two reduction steps, was corroborated by GC-MS analysis.

In accordance with previous reports,¹⁴ the benchmarking reduction reaction of CO₂ with Et₃SiH under our experimental conditions ([B]₀ = [Al]₀ = 5 mol %, C₆D₃Br, 25 or 80 °C, 1 or 6 bar of CO₂) was not productive with B(C₆F₅)₃ (Table S2, entries 1–3), and the same reaction with Al(C₆F₅)₃(toluene)_{0.5} (entry 4) resulted in a poor conversion of hydrosilane (16%)

Table 4. Catalytic Reduction of CO₂ with Et₃SiH in the Presence of 1-Al^a

entry	precat. (mol %)	silane/conversn (%) ^b	solvent	P _{CO₂} (bar)	T (°C)	t (h)	Si product conversn (%) ^c				
							a	b	c	d	f + g
1	1-Al (10)	Et ₃ Si-H/0	C ₆ D ₅ Br	1	80	48	0	0	0	0	0
2	1-Al (5.0), B(C ₆ F ₅) ₃ (5.0)	Et ₃ Si-H/84	C ₆ D ₅ Br	1	80	5	0	4.7	0.2	74.3	2.7
3	1-Al (5.0), B(C ₆ F ₅) ₃ (5.0)	Et ₃ Si-H/>98	C ₆ D ₅ Br	1	80	10	0	0	0.2	94.6	3.1
4 ^d	1-Al (5.0), B(C ₆ F ₅) ₃ (5.0)	Et ₃ SiH/>98	C ₆ D ₅ Br	6	80	5	0	28.6	0.3	53.7	7.2
5	1-Al (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/54	C ₆ D ₅ Br	1	25	48	0	0.7	0.5	47.0	2.1
6	1-Al (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/27	C ₆ D ₆	1	25	48	0	2.6	0	17.4	2.4
7 ^d	1-Al (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/>98	C ₆ D ₅ Br	6	25	30	0	1.2	0	91.6	2.9
8 ^d	1-Al (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/97	C ₆ D ₆	6	25	30	0	16.7	0.2	67.4	5.0
9 ^d	1-Al (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/>98	C ₆ D ₅ Br	6	80	5	0	40.1	1.9	46.0	4.8
10 ^d	1-Al (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/10	C ₆ D ₆	6	80	5	0	5.7	0	0.1	1.9
11 ^d	1-Al (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/>98	C ₆ D ₆	6	80	15	0	50.2	0.8	38.6	4.9
12 ^d	1-Al (0.5), B(C ₆ F ₅) ₃ (1.5)	Et ₃ Si-H/71	C ₆ D ₆	6	25	48	0	3.4	0	63.5	1.6
13 ^d	1-Al (1.5), B(C ₆ F ₅) ₃ (0.5)	Et ₃ Si-H/96	C ₆ D ₆	6	25	48	0	30.0	0.7	53.9	4.5
14 ^d	1-Al (0.5), B(C ₆ F ₅) ₃ (1.5)	Et ₃ Si-H/48	C ₆ D ₆	6	80	13	0	29.9	0.7	9.0	5.1
15 ^d	1-Al (1.5), B(C ₆ F ₅) ₃ (0.5)	Et ₃ Si-H/90	C ₆ D ₆	6	80	13	0	60.1	0.8	11.6	8.7
16	1-Al (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/10	C ₆ D ₅ Br	1	80	5	1.6	0.5	1.1	trace	0
17	1-Al (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/15	C ₆ D ₅ Br	1	80	48	1.2	0.7	0	trace	0.5
18 ^d	1-Al (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/15	C ₆ D ₅ Br	6	80	5	1.4	0.4	2.8	trace	0
19 ^d	1-Al (5.0), Al(C ₆ F ₅) ₃ (toluene) _{0.5} (5.0)	Et ₃ Si-H/23	C ₆ D ₅ Br	6	80	48	0.9	0.8	1.0	trace	0

^aReaction conditions, unless otherwise stated: solvent (0.5 mL), [Si-H]₀ = 0.26 mol L⁻¹, [cat.]₀ = 0.013 mol L⁻¹, n(CO₂)₀ = 1.3 × 10⁻⁴ mol, internal standard (hexamethylbenzene) 0.0616 mol L⁻¹. ^bConversion of hydrosilane determined by the integration of the ¹H NMR resonances vs those of the standard, hexamethylbenzene. ^cYield of Si product determined by the integration of the corresponding ¹H NMR peak vs those of the standard, hexamethylbenzene. ^dSolvent (0.1 mL), [Si-H]₀ = 0.54 mol L⁻¹, [Cat]₀ = 0.054 mol L⁻¹, n(CO₂)₀ = 3.2 × 10⁻⁴ mol, internal standard (hexamethylbenzene) = 0.0615 mol L⁻¹.

toward **a** (<1%) and **b** (15%). Upon using the tandem system B(C₆F₅)₃/Al(C₆F₅)₃(toluene)_{0.5}¹⁴ (entries 5–7), the reduction appeared to be somewhat slower under our experimental conditions, and high hydrosilane conversions and methane yields (>80 and >70%, respectively) were achieved at 6 bar of CO₂ pressure after 48 h (entry 7).

All single-component systems **1-M** appeared to be either completely inactive (M = Ga, In, Zn) or only sluggishly active (M = B, Al) in the reduction of CO₂ (1 bar) with Et₃SiH, attempted in both C₇D₈ and in C₆D₅Br (Table 3, entries 1–3; Table 4, entry 1; Table S3, entries 1, 6, and 10). Therefore, their two-component combinations with B(C₆F₅)₃ or Al(C₆F₅)₃(toluene)_{0.5} were systematically studied as precatalysts (Tables 3 and 4 and Table S3). With the binary system **1-B**/B(C₆F₅)₃ in C₆D₅Br, the three products observed by ¹H NMR spectroscopy (entries 4–7, Table 3)⁴⁰ are the major (Et₃SiO)₂CH₂ (**b**) and methane (**d**) and the minor Et₃SiOCH₃ (**c**); no formation of the primary reduction product, silyl formate Et₃SiOC(O)H (**a**), was observed in any of the cases, regardless of the conditions. On the other hand, with the congener **1-B**/Al(C₆F₅)₃(toluene)_{0.5}, only products **b** and **d** were detected.⁴¹ These results are not surprising and in previous studies using various catalytic systems have been explained by an extremely high activity of **a** toward reduction with Et₃SiH.^{3f,6,16}

Comparable activities were found for **1-B**/B(C₆F₅)₃ and **1-B**/Al(C₆F₅)₃(toluene)_{0.5} at 80 °C and at both 1 and 6 bar of CO₂ pressure (compare Table 3, entries 5/6 vs 8/10, respectively). At the same time, a complete hydrosilane conversion was achieved with **1-B**/B(C₆F₅)₃, at least 2 times faster than that with **1-B**/Al(C₆F₅)₃(toluene)_{0.5} under the same conditions (compare entries 7 and 11).

The attempt to perform the reduction reaction under conditions potentially generating a FLP^{21b,42} upon using an

equimolar mixture of **1-B** and tBu₃P failed (Table 3, entry 12). No conversion of Et₃SiH was observed in this case, and no products were detected.

Astonishingly, the binary system **1-Al**/B(C₆F₅)₃ appeared to be the most active within the whole series of combinations (Table 4). With this system, a complete hydrosilane conversion can be achieved within 5–10 h at 80 °C at both 1 and 6 bar of CO₂ pressure (entries 2–4). By analogy with **1-B**/B(C₆F₅)₃, the same three products were detected by ¹H NMR spectroscopy: the major **b** and **d** and the minor **c**. The congener **1-Al**/Al(C₆F₅)₃(toluene)_{0.5} (entries 16–19) provided a low conversion (<25%) of Et₃SiH, which could be achieved at 80 °C and at 6 bar only after 48 h, affording small amounts of **a**–**c** and traces of **d**.

Therefore, the mixed catalytic system **1-Al**/B(C₆F₅)₃ was successfully applied using a lower loading ([Al]₀ = [B]₀ = 1 mol %). Though moderate conversion of hydrosilane was obtained at room temperature and 1 bar of CO₂ pressure in C₆D₅Br or in C₆D₆ (Table 4, entries 5 and 6, respectively), at higher pressure (6 bar; entries 7 and 8, respectively; Figure S22) Et₃SiH was completely consumed within a shorter period of time (30 h). At higher temperature (80 °C) and 6 bar of CO₂ pressure, the complete consumption of hydrosilane can be achieved within 5 h in C₆D₅Br and within 10 h in C₆D₆ (entries 9 and 11, respectively). In order to probe the critical role of **1-Al** as a cocatalyst, a series of experiments with different respective cocatalyst ratios was conducted (entries 12–15). Thus, upon using a larger proportion of **1-Al** ([**1-Al**]₀/[B(C₆F₅)₃]₀ = 3/1, entries 13 and 15), the high silane conversion was achieved more quickly and the yield of **b** was systematically higher. This argues in favor of the predominant contribution of **1-Al** in the generation of catalytically active species responsible for the conversion of Et₃SiH to **b**.

Under the optimized conditions ($[1\text{-Al}]_0/[B(C_6F_5)_3]_0 = 1$ mol %, C_6D_6 , 6 bar, $80^\circ C$), hydrosilylation of CO_2 with various hydrosilanes was then studied (Table 5). The

Table 5. Catalytic Reduction of CO_2 with Different Hydrosilanes in C_6D_6 at $80^\circ C$ and 6 bar in the Presence of $1\text{-Al}/B(C_6F_5)_3$ ($[Al]_0 = [B]_0 = 1$ mol %)^a

entry	silane/conversn (%) ^b	<i>t</i> (h)	Si product conversn (%) ^c				
			a	b	c	d	f + g
1	Et ₃ SiH/10	5	0	5.7	0	0.1	1.9
2	PhMe ₂ SiH/75	5	0	0	0	56.1	5.8
4	PhSiH ₃ /63	48	0	4.7	4.6	16.2	5.9
3	Ph ₂ SiH ₂ /35	48	0	31.1	0.8	0	1.1
5	Ph ₃ SiH/5	48	0	0	0	0	1.5
6	(EtO) ₃ SiH/0	48	0	0	0	0	0

^aReaction conditions: solvent (0.1 mL), $[Si\text{-H}]_0 = 0.54$ mol L⁻¹, $[cat.]_0 = 0.054$ mol L⁻¹, $n(CO_2)_0 = 3.2 \times 10^{-4}$ mol, internal standard (hexamethylbenzene) 0.0615 mol L⁻¹. ^bConversion of hydrosilane determined by the integration of the ¹H NMR resonances vs those of the standard, hexamethylbenzene. ^cYield of Si product determined by the integration of the corresponding ¹H NMR peak vs those of the standard, hexamethylbenzene.

composition of each crude reaction mixture was determined by ¹H NMR spectroscopy. Thus, the following hydrosilane reactivity trend was revealed: PhMe₂SiH > Et₃SiH > PhSiH₃ > Ph₂SiH₂ > Ph₃SiH > (EtO)₃SiH. The observed trend is only partially in agreement with both thermodynamic hydricity (Ph₃SiH = PhMe₂SiH > Et₃SiH > Ph₂SiH₂ > PhSiH₃)⁴³ and kinetic nucleophilicity (PhMe₂SiH > Et₃SiH > Ph₃SiH > Ph₂SiH₂ > PhSiH₃ > (EtO)₃SiH)⁴⁴ tendencies and is inconsistent with those for the series of relatively bulkier hydrosilanes Ph₃SiH, Ph₂SiH₂, and PhSiH₃, which demonstrate quite the opposite corresponding trends. Given that the observed trend can only be rationalized in part in terms of the thermodynamic and kinetic stability of the corresponding R₃SiH-LA adducts (LA = Lewis acid, e.g. B(C₆F₅)₃) responsible for the hydride transfer,^{14,15} we surmised that the steric hindrance of hydrosilanes also contributes to the stability of the titular key adducts and, thus, to the global activity.

The reactions with PhMe₂SiH and PhSiH₃ afforded methane (d) as the major product, while in the presence of Ph₂SiH₂, mostly b was obtained.

Within the series of combinations **1-M**/ $B(C_6F_5)_3$ (M = Ga, In, Zn; Table S3), the highest activity in hydrosilylation of CO_2 with Et₃SiH was observed with **1-In**/ $B(C_6F_5)_3$. For instance, a result comparable with that of **1-Al**/ $B(C_6F_5)_3$ (Table 4, entry 9) was obtained with **1-In**/ $B(C_6F_5)_3$ in C_6D_5Br at $80^\circ C$ and 6 bar of CO_2 pressure—a full conversion of hydrosilane within 13 h affording mostly b and d (Table S3, entry 8). In C_6D_6 , the same reaction was less efficient, resulting only in 43% of Et₃SiH consumed (entry 9).

The binary **1-Zn**/ $B(C_6F_5)_3$ system ($[Zn]_0 = [B]_0 = 5$ mol %) was also probed in C_6D_5Br at $80^\circ C$ and 1 or 6 bar of CO_2 pressure (Table S3; entries 11–14). At higher pressure, 57% conversion of hydrosilane was achieved within the first 5 h (entry 13). However, prolonged heating of the reaction mixture resulted only in 67% conversion at most after 2 days (entry 14), thus suggesting deactivation of the catalytic system. Interestingly, among the three observed products of CO_2 reduction (b–d), Et₃SiOCH₃ (c) was systematically the major product.

Kinetic and Mechanistic Studies of Hydrosilylation: Catalyst Transformation. A closer inspection of the NMR data obtained for the reaction mixtures through the series of catalytic tests (Tables 3–5 and Table S3) revealed the systematic presence of the two resonances in a ca. 1/3 ratio in the aliphatic region of the corresponding ¹H NMR spectra: broad (δ 3.20 or 3.02 ppm) and sharp (δ 2.69 or 2.56 ppm) singlets in C_6D_5Br or C_6D_6 , respectively. These two signals were assigned to the two *N*-silyl-aniline compounds (C₆F₅)-N(*H*)SiEt₃ (f) and (C₆F₅)N(*Me*)SiEt₃ (g); in addition, their nature was confirmed by GC-MS analysis (Figures S23 and S24, respectively).

To gain a better insight into a possible mechanism of hydrosilylation of CO_2 with Et₃SiH and to address the role of f and g in the catalytic process, we carried out a series of kinetic studies with the most efficient tandem system, **1-Al**/ $B(C_6F_5)_3$. Thus, the consumption of Et₃SiH and formation of products a–d and of compounds f and g were monitored by ¹H NMR spectroscopy under regular conditions (Figure 5) and also at

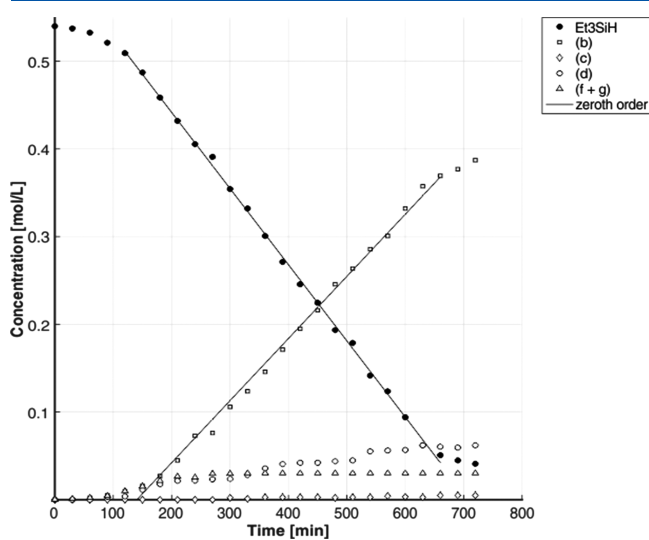


Figure 5. Kinetic plot of concentration (mol L⁻¹) as a function of time (min) for reduction of CO_2 with Et₃SiH at $80^\circ C$ and 6 bar of CO_2 pressure: solvent C_6D_6 (0.1 mL), $[Et_3SiH]_0 = 0.54$ mol L⁻¹, $[1\text{-Al}]_0 = 0.054$ mol L⁻¹, $[B(C_6F_5)_3] = 0.054$ mol L⁻¹, $n(CO_2) = 3.2 \times 10^{-4}$ mol, internal standard (hexamethylbenzene) 0.0615 mol L⁻¹; $k_{app,[SiH]} = 1.45(7) \times 10^{-5}$ M s⁻¹, $R^2 = 0.999$, $k_{app,[b]} = 1.2(1) \times 10^{-5}$ M s⁻¹, $R^2 = 0.994$.

different temperatures (Figure S25a–d). First, the reaction exhibited an induction period featuring a slow consumption of Et₃SiH and a gradual formation of products b–d with a slow appearance of silyl-anilines f and g. In previous studies on hydrosilylation of CO_2 ,^{15a,45} a similar induction period was observed and attributed^{15a} to a slow process of the reorganization of the poorly active associated ion pair $[Cp^*_2Sc]^+[HC(O)OB(C_6F_5)_3]^-$, derived from precatalyst $[Cp^*_2Sc]^+[HB(C_6F_5)_3]^-$ and CO_2 , into a significantly more catalytically efficient separated ion pair $[Cp^*_2Sc(b)]^+[HC(O)OB(C_6F_5)_3]^-$, that is triggered in the presence of bis(silyl)acetal b. In our case, the existence of the induction period can also be related to a catalyst evolution process that is accompanied by elimination of silyl-anilines f and g. In order to address this hypothesis, a kinetic experiment was performed using the catalytic system **1-Al**/ $B(C_6F_5)_3$ aged at room temperature in C_6D_6 for 12 h in the presence of Et₃SiH.

Prior to the addition of CO₂ (6 bar), the reaction featured ca. 19% hydrosilane depletion and contained 4% of **f** and **g**. The subsequent process proceeded at 80 °C without an induction period (Figure S27a) and, after 6 h, resulted in formation of **b** in 70% yield and with nearly complete conversion of hydrosilane.

After the initiation step, both the depletion of Et₃SiH and the formation of **b** appeared to obey zero-order kinetics (Figure S25b–d). This finding of the overall zero order in hydrosilane consumption parallels the behavior of [Cp*₂Sc]⁺[HB(C₆F₅)₃][−] precatalyst that was explained by the existence of a rate-determining step related to the formation of a key intermediate without an immediate participation of hydrosilane.^{15a} The fact that in our case the rates of hydrosilane depletion and formation of **b** are not systematically equal and are both independent of the corresponding reactant/product concentrations may be diagnostic of a complicated multistep mechanism operating with this catalytic system, where each reduction step can be catalyzed by a different species. Eyring analyses of the kinetic data (Figure S26) provided the corresponding free energy barrier value (ΔG[‡]₂₉₈ of 25(2)–27(2) kcal mol^{−1}), which is comparable to those evaluated computationally for the prototype tandem system Al(C₆F₅)₃/B(C₆F₅)₃ (ΔG[‡]₂₉₈ of 20–22 kcal mol^{−1}).¹⁴

The origin of silyl-anilines **f** and **g** was deduced from several independent stoichiometric experiments. First, addition of B(C₆F₅)₃ (1 equiv) to **1-H** in C₆D₆ or in C₆D₅Br resulted in a change in chemical shifts of the ¹H and ¹⁹F{¹H} NMR signals and their pattern for both reagents, which is in agreement with a possible formation of the adduct (**1-H**)·B(C₆F₅)₃.⁴⁶ Subsequent addition of excess Et₃SiH after 20 h at 80 °C afforded a complete conversion of **1-H** to an equimolar mixture of **f** and **g** (Figure S28).⁴⁷ However, this pathway is unlikely the source of **f** and **g**, provided the experiments were carried out under an inert atmosphere and, thus, the preliminary hydrolysis of **1-Al** can be excluded.

While no reaction was observed between **1-Al** and B(C₆F₅)₃ in C₆D₅Br or in C₆D₆ at 80 °C, addition of Et₃SiH (20 equiv) resulted in a complete consumption of B(C₆F₅)₃ and formation of an unidentified product (Figure S29). The same combination of **1-Al** and B(C₆F₅)₃ and Et₃SiH (20 equiv) in the presence of CO₂ (20 equiv at 1 bar of pressure) exhibited a complete consumption of hydrosilane after 20 h at 80 °C, affording a complex mixture of unreacted **1-Al** and B(C₆F₅)₃, silyl-anilines **f** and **g**, CH₄ (**d**), and some unidentified products (Figure S30). In an attempt to isolate intermediates of this reduction reaction, the corresponding reaction mixture was subjected to crystallization in toluene. Gratifyingly, a new compound, the B(C₆F₅)₃ adduct of *N*-silyl-formamidate **1-SiEt₃** ({B(C₆F₅)₃}·**1-SiEt₃**),⁴⁸ was isolated, whose identity was established by X-ray diffraction analysis (Figure 6). On the other hand, all attempts to obtain exploitable NMR data for the crystals of this compound failed due to its remarkable instability in solution.⁴⁹ The formation of {B(C₆F₅)₃}·**1-SiEt₃** likely resulted from the putative process of a B(C₆F₅)₃-assisted reduction of **1-Al** with Et₃SiH leading to **1-SiEt₃** and an unidentified aluminum hydrido species, followed by coordination of the former with B(C₆F₅)₃.^{22,46,50} All attempts to isolate and authenticate aluminum-containing intermediates and products of this reaction have been unsuccessful so far.

It should be mentioned that in the above reactions the formation of such typical products of the reaction of Et₃SiH

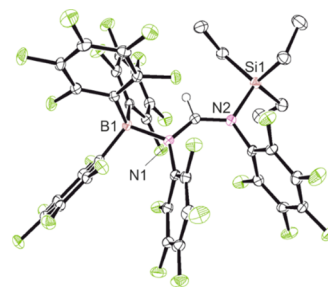


Figure 6. Molecular structure of {B(C₆F₅)₃}·**1-SiEt₃**.

with B(C₆F₅)₃ as Et₃Si-H·B(C₆F₅)₃,^{51,52} HB(C₅F₅)₂,⁵³ Et₃Si-(C₆F₅)₂,^{51b,52,54} and {B(C₆F₅)₃}·Et₃SiOC(O)H¹⁴ either was not observed or could not be unequivocally corroborated.

A series of CO₂ hydrosilylation experiments was attempted using proligand **1-H** in combination with B(C₆F₅)₃ or Al(C₆F₅)₃(toluene)_{0.5} (Table 6). The hydrosilylation reaction was not operational in the presence of only **1-H** (entry 1), whereas upon addition of B(C₆F₅)₃ as a cocatalyst, a nearly half conversion of hydrosilane was achieved over 24 h at 80 °C and 6 bar of CO₂ pressure both in C₆D₅Br and in C₆D₆ (entries 3 and 4, respectively). However, the metal-free system **1-H**/B(C₆F₅)₃ appeared to be substantially less efficient than **1-Al**/B(C₆F₅)₃ (compare with entries 9 and 11 in Table 4, respectively), also providing larger amounts of methane (**d**) in these experiments. In all experiments, the formation of significant amounts of anilines **f** and **g** was detected, apparently derived from the reduction processes. Under the same experimental conditions, the congener **1-H**/Al-(C₆F₅)₃(toluene)_{0.5} was found to be completely inactive (entry 5). Also, the *in situ* combination of **1-SiEt₃**/B(C₆F₅)₃, probed under the same conditions (C₆D₆, 80 °C, 6 bar) as those enabling the higher performances with **1-Al**/B(C₆F₅)₃ (Table 4, entry 11), resulted only in 23% conversion of hydrosilane after 48 h (entry 6), giving methane as the principal product (17%).

The above observations suggest that the binary catalytic systems obtained upon combining **1-M** (M = B, Al, Ga, In, Zn) with E(C₆F₅)₃ are susceptible of reacting with Et₃SiH, thus releasing **1-SiEt₃**, which then follows a prompt reduction to afford products **f** and **g**. These two *N*-silyl-anilines, as well as **1-SiEt₃** itself, in combination with B(C₆F₅)₃ can also constitute catalytically active systems capable of CO₂ hydrosilylation reactions as tandem FLP-like R₃N/B(C₆F₅)₃ analogues.⁷ On the other hand, the nature of other Al-containing products derived from **1-Al**, which are apparently responsible for the predominant formation of **b**, could not be established so far.

CONCLUSIONS

In this study, a series of homoleptic group 13 (**1-B,Al,Ga,In**) and group 12 (**1-Zn**) complexes incorporating electron-withdrawing formamidate ligands was synthesized. Their solution and solid-state structures were established using NMR techniques and XRD analysis, respectively. The higher Lewis acidic character of **1-B** in comparison to that of B(C₆F₅)₃ was established using both experimental and computational techniques.

The obtained complexes were studied as precursors for CO₂ reduction using hydrosilanes as reducing agents. While the single-component **1-M** exhibited no or very poor activity in hydrosilylation, the two-component systems derived from **1-M**

Table 6. Catalytic Reduction of CO₂ with Et₃SiH in the Presence of 1-H and 1-SiEt₃^a

entry	precat. (mol %)	silane/conversn (%) ^b	solvent	P _{CO₂} (bar)	T (°C)	t (h)	Si product conversn (%) ^c				
							a	b	c	d	f + g
1 ^d	1-H (10.0)	Et ₃ Si-H/0	C ₆ D ₅ Br	6	80	48	0	0	0	0	0
2	1-H (6.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/21	C ₆ D ₅ Br	1	80	24	0	0.6	0	0	10.0
3 ^d	1-H (6.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/44	C ₆ D ₅ Br	6	80	24	0	1.6	0	20.1	7.4
4 ^d	1-H (6.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/49	C ₆ D ₆	6	80	24	0	3.8	0	26.4	6.4
5 ^d	1-H (6.0), Al(C ₆ F ₅) ₃ (tol) _{0.5} (1.0)	Et ₃ Si-H/0	C ₆ D ₅ Br	6	80	24	0	0	0	0	0
6 ^d	1-SiEt ₃ (1.0), B(C ₆ F ₅) ₃ (1.0)	Et ₃ Si-H/23	C ₆ D ₆	6	80	48	0	3.9	0	17.3	0.3

^aReaction conditions, unless otherwise stated: solvent (0.5 mL), [Si-H]₀ = 0.26 mol L⁻¹, [cat.]₀ = 0.013 mol L⁻¹, n(CO₂)₀ = 1.3 × 10⁻⁴ mol, internal standard (hexamethylbenzene) 0.0616 mol L⁻¹. ^bConversion of hydrosilane determined by the integration of the ¹H NMR resonances vs those of the standard, hexamethylbenzene. ^cYield of Si product determined by the integration of the corresponding ¹H NMR peak vs those of the standard, hexamethylbenzene. ^dSolvent (0.1 mL), [Si-H]₀ = 0.54 mol L⁻¹, [cat.]₀ = 0.054 mol L⁻¹, n(CO₂) = 3.2 × 10⁻⁴ mol, internal standard (hexamethylbenzene) 0.0615 mol L⁻¹.

and E(C₆F₅)₃ (E = B, Al) were found to be significantly more active. Among them, the binary combination 1-Al/B(C₆F₅)₃ showed the best performance within the whole series, thus providing high hydrosilane (Et₃SiH) conversions over a range of conditions (P_{CO₂}, temperature, benzene or bromobenzene solvent). The main products of these reactions are CH₂(OSiEt₃)₂ (b) and CH₄ (d), while the product ratio was found to be dependent on the reaction conditions. Other hydrosilanes (PhSiMe₂H, PhSiH₃, and Ph₂SiH₂) were also successfully employed for CO₂ hydrosilylation with 1-Al/B(C₆F₅)₃ under the optimized conditions.

Transformation of the initial catalytic precursors to afford multiple species was evidenced by kinetic and mechanistic studies. In particular, the hydrosilane/B(C₆F₅)₃-assisted cleavage of the ligand–metal bond in the formamidinate precursor 1-M (M = Al), affording *N*-silyl-formamidine 1-SiEt₃, is surmised to be one of the key steps toward the formation of so far unidentified aluminum-based species featuring a better catalytic performance in the hydrosilylation of CO₂. At the same time, different N-bases, namely (C₆F₅)N(H)SiEt₃ and (C₆F₅)N(Me)SiEt₃, concomitantly generated from the precursor on the initiation step can also participate as the FLP partners to B(C₆F₅)₃ and thus interfere as cocatalysts in several different reduction steps of hydrosilylation. Understanding the behavior of a catalytic system and factors (steric and electronic) responsible for its stability and performance will allow rational engineering of new, more efficient and selective molecular catalysts for chemical transformations of CO₂. These investigations are underway in our laboratories.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF, Et₂O) and Na/K alloy (toluene, pentane) under argon, degassed thoroughly, and stored under argon prior to use. Deuterated solvents (C₆D₆, C₇D₈, THF-*d*₆; >99.5% D, Deutero GmbH and Euroisotop) were vacuum-transferred from Na/K alloy into storage tubes. CDCl₃, CD₂Cl₂, and C₆D₅Br were kept over CaH₂ and vacuum-transferred before use. CO₂ (Air Liquide, 99.99%) was additionally dried over molecular sieves (Sertronic 500 T DB) prior to utilization. Base-free B(C₆F₅)₃ was obtained by sublimation of the adduct (Et₂O)·B(C₆F₅)₃⁵⁵ under high dynamic vacuum. Al(C₆F₅)₃(toluene)_{0.5},⁵⁶ 1-H,²³ a,¹⁴ b,⁵⁷ and c¹⁴ were prepared according to literature protocols. Other starting materials were purchased from Alfa, Strem, Acros, or Aldrich, and used as received.

Instruments and Measurements. NMR spectra of complexes were recorded on Bruker AM-400 and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C, unless otherwise indicated. ¹H NMR chemical shifts are reported in ppm vs SiMe₄ using the residual solvent resonances. ¹⁹F NMR chemical shifts were determined by external reference to an aqueous solution of NaBF₄. ¹¹B NMR spectra were referenced to external BF₃·OEt₂. Assignment of resonances was made from 2D ¹H–¹H COSY, ¹H–¹³C HSQC, and HMBC NMR experiments. Coupling constants are given in hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations.

Synthesis of B(NCN)₃. In the glovebox, 1-H (5.02 g, 13.3 mmol) and potassium hydride (0.80 g, 19.9 mmol) were placed into a Schlenk tube equipped with a magnetic stirrer. Dry THF (30 mL) was added under argon, and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered and all the volatiles were removed under vacuum. The crude potassium salt of the ligand was dried under vacuum for 4 h, and dry Et₂O (30 mL) was added followed by addition of BCl₃ (4.45 mL, 13.3 mmol, a 1 M solution in CH₂Cl₂). The mixture was stirred at room temperature overnight and then filtered and concentrated to half of the initial volume. The solid was crystallized at room temperature by addition to this solution of dry heptane (4 mL). Off-white crystals were separated and dried under vacuum to afford a pinkish powder of 1-B (2.36 g, 2.1 mmol, 80%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 8.27 (s, 3H, CH). ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz, 25 °C): δ -148.55 (br m, 12F, C₆F₅), -155.75 (br m, 6F, C₆F₅), -162.18 (br m, 12F, C₆F₅). ¹³C{¹H} NMR (CD₂Cl₂, 400 MHz, 25 °C) (some signals from quaternary carbons were not identified): δ 153.4 (s, CH), 142.3 (br d, ¹J = 250, *o*-C₆F₅), 140.5 (br d, ¹J = 255, *p*-C₆F₅), 139.1 (br d, ¹J = 250, *m*-C₆F₅). Anal. Calcd for C₃₉H₃BF₃₀N₆: C, 41.23; H, 0.27; N, 7.40. Found: C, 41.16; H, 0.26; N, 7.33.

Synthesis of Al(NCN)₃ (1-AI). To a solution of 1-H (1.0 g 2.6 mmol) in toluene (5 mL) was added trimethylaluminum (1 M solution in heptane, 0.89 mL, 0.89 mmol). The reaction mixture was stirred at room temperature overnight. All volatiles were evaporated in vacuo, and the crude product was recrystallized from toluene to give white crystals of 1-AI (0.89 g, 0.77 mmol, 87%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 7.75 (s, 3H, CH). ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz, 25 °C): δ -153.45 (d, ¹J = 20.7, 12F, *o*-C₆F₅), -159.85 (t, ¹J = 22.6, 6F, *p*-C₆F₅), -162.88 (t, ¹J = 42.1, 12F, *m*-C₆F₅). ¹³C{¹H} NMR (CD₂Cl₂, 400 MHz, 25 °C) (some signals from quaternary carbons were not identified): δ 153.1 (s, CH), 141.4 (br d, ¹J = 247, *o*-C₆F₅), 138. Six (br d, ¹J = 251, *m*-C₆F₅). Anal. Calcd for C₃₉H₃AlF₃₀N₆: C, 40.65; H, 0.26; N, 7.29. Found: C, 40.62; H, 0.25; N, 7.23.

Synthesis of Ga(NCN)₃ (1-Ga). Using a protocol similar to that described for 1-B, compound 1-Ga was obtained from 1-H (3.0 g, 7.8 mmol), KH (0.50 g, 13 mmol) and GaCl₃ (0.47 g, 2.6 mmol). 1-Ga was isolated as a slightly pink solid (0.37g, 0.31 mmol, 12%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 7.66 (s, 3H, CH). ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz, 25 °C): δ -153.28 (d, ¹J = 22.0, 12F, *o*-C₆F₅),

–159.86 (t, $J = 22.0$, 6F, *p*-C₆F₅), –162.88 (t, $J = 22.0$, 12F, *m*-C₆F₅). Numerous attempts to obtain the ¹³C NMR data for this compound failed; only signals from the solvent were observed in the corresponding NMR spectra. Anal. Calcd for C₃₉H₃GaF₃₀N₆: C, 39.19; H, 0.25; N, 7.03. Found: C, 39.22; H, 0.27; N, 7.14.

Synthesis of In(NCN)₃ (1-In). Using a protocol similar to that described for 1-B, compound 1-In was obtained from 1-H (3.0 g, 7.8 mmol), KH (0.50 g, 13 mmol) and InBr₃ (0.92 g, 2.6 mmol). 1-In was isolated as a pink powder (0.36 g, 0.29 mmol, 11%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 8.20 (s, 3H, CH). ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz, 25 °C): δ –154.23 (d, $J = 21.4$, 12F, C₆F₅), –160.69 (t, $J = 21.4$, 6F, C₆F₅), –162.77 (t, $J = 21.4$, 12F, C₆F₅). ¹³C{¹H} NMR (CD₂Cl₂, 400 MHz, 25 °C): δ 164.6 (s, CH), 142.0 (br d, $^1J = 250$, *o*-C₆F₅), 140.5 (br d, $^1J = 255$, *m*-C₆F₅), 137.0 (br d, $^1J = 250$, *p*-C₆F₅), 119.9 (br s, *ipso*-C₆F₅). Anal. Calcd for C₃₉H₃InF₃₀N₆: C, 37.77; H, 0.24; N, 6.78. Found: C, 38.01; H, 0.29; N, 6.98.

Synthesis of Zn(NCN)₂ (1-Zn). Using a protocol similar to that described for 1-Al, compound 1-Zn was obtained from 1-H (3.0 g, 7.8 mmol) and Et₂Zn (1 M in heptane, 2.67 mL, 2.67 mmol) and isolated as a transparent crystalline solid (1.8 g, 2.1 mmol, 83%). ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ 7.93 (s, 2H, CH) ppm. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz, 25 °C): δ –152.97 (br m, 8F, C₆F₅), –160.04 (br m, 4F, C₆F₅), –162.41 (t, $J = 20.8$, 8F, C₆F₅). ¹³C{¹H} NMR (C₆D₆, 400 MHz, 25 °C) (some signals from quaternary carbons were not identified): δ 169.03 (s, CH), 141.8 (br d, $^1J = 246$, *o*-C₆F₅), 137.9 (br d, $^1J = 248$, *m*-C₆F₅), 120.6 (br s, *ipso*-C₆F₅). Anal. Calcd for C₂₆H₂F₂₀N₄Zn: C, 38.28; H, 0.25; N, 6.87. Found: C, 38.34; H, 0.30; N, 7.01.

Synthesis of Et₃Si(NCN) (1-SiEt₃). In the glovebox, 1-H (0.50 g, 1.3 mmol) and KH (0.09 g, 2.0 mmol) were placed into a Schlenk tube equipped with a magnetic stirrer. Dry THF (15 mL) was added under argon, and the reaction mixture was stirred at room temperature. After 12 h, the reaction mixture was filtered and all the volatiles were removed under vacuum. The crude potassium salt was dried under vacuum for 4 h, and dry toluene (15 mL) was added followed by addition of Et₃SiCl (2.25 mL, 1.3 mmol) at –78 °C. The mixture was stirred overnight at room temperature and then filtered. All volatiles were removed, and a brownish oily product was obtained and then dried under vacuum overnight to give 1-SiEt₃ (0.03 g, 0.55 mmol, 42%). The compound apparently exists as a ca. 1/0.9 mixture of two atropoisomers arising from a congested rotation around the C–N single bond (Figure S19),⁵⁸ which slowly interconvert at room temperature. ¹H NMR (C₇D₈, 400 MHz, 25 °C): δ 7.66 (br s, 1H, CH), 0.86 (br m, 9H, CH₃CH₂), 0.59 (br m, 6H, CH₃CH₂). ¹⁹F{¹H} NMR (C₇D₈, 376.5 MHz, 25 °C): δ –145.9 (br m C₆F₅), –155.2 (br m, C₆F₅), –155.5 (t, $J = 18.8$, C₆F₅), –162.8 (br m, C₆F₅), –164.6 (m, C₆F₅). ¹³C{¹H} NMR (C₇D₈, 400 MHz, 25 °C) (some signals from quaternary carbons were not identified): δ 156.6 (br s, 1C, CH), 144.9 (br d, $^1J = 246$, *o*-C₆F₅), 141.1 (br d, $^1J = 251$, *o*-C₆F₅), 140.8 (br d, $^1J = 251$, *p*-C₆F₅), 138.3 (br d, $^1J = 251$, *m*-C₆F₅), 137.3 (br d, $^1J = 251$, *p*-C₆F₅), 6.4 (s, CH₃CH₂), 4.0 (s, CH₃CH₂). Despite repeated attempts, a reproducible and satisfactory elemental analysis for 1-SiEt₃ (C₁₉H₁₆F₁₀N₂Si) could not be obtained, apparently due to the extreme air and moisture sensitivity of the compound and possible formation during pyrolysis of nonpyrolyzable silicon carbide.

General Procedure for CO₂ Hydrosilylation: NMR-Scale Reactions. Reaction at 1 bar of CO₂ Pressure. In the glovebox, a Teflon-valved NMR tube was charged with the internal standard hexamethylbenzene (5.0 mg, 0.0308 mmol), HSiEt₃ (21 μL, 0.13 mmol), precatalyst (6.15 × 10^{–3} mmol; 5.0 mol % vs hydrosilane), and, when relevant, a solution of E(C₆F₅)₃ (5.0 mol % vs hydrosilane). Then, dry degassed C₆D₃Br or C₆D₆ (0.5 mL) was added, and the NMR tube was sealed. The tube was degassed by two freeze–pump–thaw cycles and charged with pure CO₂ under 1 bar of pressure (0.13 mmol). Afterward, it was introduced in the NMR spectrometer preset at the desired temperature. The progress of the reaction was monitored by NMR spectroscopy.

Reaction at 6 bar of CO₂ Pressure. In the glovebox, a Wilmad high-pressure Teflon-valved NMR tube was charged with the internal standard hexamethylbenzene (1.0 mg, 0.00616 mmol), HSiEt₃ (8.6

μL, 0.054 mmol), a dilute solution of the precatalyst (5.4 × 10^{–4} mmol; 1.0 mol % vs hydrosilane), the relevant E(C₆F₅)₃ (1.0 mol % vs hydrosilane), and dry degassed C₆D₃Br or C₆D₆ (0.1 mL). Then the NMR tube was sealed. The tube was degassed by two freeze–pump–thaw cycles and charged with pure CO₂ under 6 bar of pressure (0.32 mmol). Afterward, it was introduced in the NMR spectrometer preset at the desired temperature. The progress of the reaction was monitored by NMR spectroscopy.

Computational Details. The calculations were performed using the Gaussian 09⁵⁹ program employing the B3PW91⁶⁰ functional and using a standard double- ξ polarized basis set: namely, the 6-31(d,p) set. The solvent effects, in our case for toluene, were taken into account during all of the calculations by means of the SMD model.⁶¹ All stationary points were fully characterized via analytical frequency calculations as either true minima (all positive eigenvalues) or transition states (one imaginary eigenvalue). The IRC procedure was used to confirm the nature of each transition state connecting two minima.⁶² Zero-point vibrational energy corrections (ZPVE) were estimated by a frequency calculation at the same level of theory, to be considered for the calculation of the total energy values. The electronic charges (at the DFT level) were computed using natural population analysis (NPA).⁶³

Crystal Structure Determination of 1-H,B,Al,Ga,In,Zn and {B(C₆F₅)₃}(1-SiEt₃). Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A combination of ω and θ scans was carried out to obtain a unique data set. The crystal structures were solved by direct methods, and the remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SIR97 and SHELXL-97).⁶⁴ Many hydrogen atoms could be located from the Fourier difference analysis. Other hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom positions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and details of data collection and structure refinement for the different compounds are given in Table S1. Crystal data and details of data collection and structure refinement for all compounds (CCDC 1950208–1950214, respectively) can be obtained from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.9b00853>.


Selected catalytic results, NMR data, and kinetic plots (PDF)

Accession Codes

CCDC 1950208–1950214 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors of this work thank ANR-17-CE06-0006-01 “CO22CHEM” for financial support. W.H. is grateful to the International Master of Molecular Catalysis and Green Chemistry program of the University of Rennes 1. Dedicated to Prof. Pierre Dixneuf on the occasion of his 80th birthday.

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